THE PREPARATION AND STEREOCHEMISTRY OF SOME INORGANIC COORDINATION COMPOUNDS

I CONFIGURATION CHANGES IN THE REACTIONS OF SOME COMPOUNDS OF COBALT AND CHROMIUM

II THE THERMAL DECOMPOSITION OF LUTEO CHROMIC SALTS

BY

THOMAS DORAN O'BRIEN

B.S., George Washington University, 1935

M.A., George Washington University, 1938

AN ABSTRACT OF A THESIS

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE OF DOCTOR OF PHILOSOPHY IN CHEMISTRY IN THE GRADUATE SCHOOL OF THE UNIVERSITY OF ILLINOIS, 1941

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There are several methods used to determine configuration in the hexacovalent coordination compounds. Examination of the easily determinable physical properties such as color or solubility is widely used, as is the resolution of the possible optical isomers. These, however, are not always applicable and other methods must be used.

It was thought that a study of the rotary dispersion curves might be used as a method of determining configuration. In molecules of the types $[Ma_4b_2]^+$ and $[MA_2b_2]^+$ (Where M is the central metal atom as cobalt or chromium, "a" is a neutral molecule as ammonia, "A" is ethylenediamine or propylenediamine, and "b" is a single negatively charged atom as chloride) cis-trans isomerism is possible and for the type $[MA_2b_2]^+$ optical isomerism is possible if the molecule is of the cis configuration. If "A" is ethylenediamine a resolution must be carried out if the rotary dispersion curve is to be determined. If, on the other hand, "A" is active propylenediamine then the molecule is optically active and the rotary dispersion curve may be determined without resort to resolution. If the groups "b" are in the trans positions, the optical rotation of the molecule will be due only to the optical rotation of the active propylenediamine and should, therefore, have approximately the same magnitude at any given wave length. It has been shown that if the "b" groups are in the cis positions, the optically active propylenediamine induces an asymmetry on the central atom, thus making the molecule itself optically active. The magnitude of optical rotation of this asymmetric molecule then, should be quite different from the magnitude of that molecule whose activity is only due to the presence of the optically active base.

It has been shown by Bailar and McReynolds,[1] that the rotary dispersion curves of levo-dichloro diethylenediamine cobaltic chloride and dichloro di-levo-propylenediamine cobaltic chloride and also of levo-carbonato diethylenediamine cobaltic ion and carbonato di-levo-propylenediamine cobaltic ion are practically identical, having the same points of maxima, minima, and zero rotation. This similarity has now been shown to hold true also in the analagous chromium compounds. It is also shown that in general when a molecule of the above type has the cis configuration, its rotary dispersion curve is quite erratic showing pronounced maxima or minima, or both; while if the molecule is of the trans configuration the curve is quite smooth with no pronounced maxima or minima.

Another method of studying configuration depends upon Walden inversion studies. Bailar and Auten[2] first realized the Walden inversion in the field of inorganic chemistry when they demonstrated that by the proper choice of reagents that either dextro or levo-carbonato dietheylenediamine cobaltic ion could be obtained from levo-dichloro diethylenediamine cobaltic ion. It was later shown that by varying only the conditions the same inversion could be accomplished. Bailar and Peppard[3], using similar conditions, failed to obtain a Walden inversion in the corresponding oxalato diethylenediamine cobaltic series.

A Walden inversion was realized, however, in the present study, in the corresponding oxalato di-dextro-propylenediamine cobaltic series. When the starting material, dichloro di-dextro-propylenediamine cobaltic chloride was dissolved in water and allowed to stand at least one hour and then added to a ten-fold excess of freshly prepared silver oxalate, the resulting oxalato salt had a specific rotation (at the D line of sodium) of +50°. If the starting material was ground dry with a ten-fold excess of silver oxalate and allowed to stand in a desiccator over potassium hydroxide for twelve hours, the resulting oxalato salt had a specific rotation of —90°. Unlike other examples of the Walden inversion in the coordination compounds both of these isomers were quite stable with respect to one another, neither one passing into the other on

prolonged heating nor on standing. These results further substantiate the hypothesis of Bailar and Peppard,[3] that the determining step in the inversion is an aquation reaction.

A third method of studying configuration, the oxidation or reduction of constituent groups in the molecule, was found to be rather limited in the study of cobalt compounds due to the ease of reduction of the central metal atom.

Pfeiffer[4] reported that if triethylenediamine chromic chloride and triethylenediamine chromic thiocyanate are heated, dichloro diethylenediamine chromic chloride and dithiocyanato diethylenediamine chromic thiocyanate respectively are formed. The dichloro salt has the cis configuration while the dithiocyanato salt has the trans. It was found that the analagous levo-propylenediamine salts yield similar products and their configurations were determined from the shapes of their rotary dispersion curves. Thermal decomposition of a large number of other salts of the same type failed to yield any well defined product, although in some cases the conditions were varied over a wide range.

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VITA

The author was born in Washington, D. C., on March 31, 1910. He was graduated from the McKinley Technical High School in February, 1927. He entered the George Washington University at the beginning of the summer sessions in June 1932 and was awarded the Bachelor of Science degree in October 1935. In June 1938 he received the Master of Arts degree from the same institution. Since June 1938 he has attended the Graduate School of the University of Illinois, holding a teaching assistantship during that time.

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